PATENT SPECIFICATION

NO DRAWINGS

822,251

Date of Application and filing Complete Specification: Aug. 26, 1957. *No. 26786/57.*

Application made in Japan on Aug. 25, 1956.

Complete Specification Published: Oct. 21, 1959.

Index at Acceptance:—Classes 37, K(1CX : 2S10 : 3X); and 82(2), E(3 : 6).
International Classification:—C23g. H01l.

COMPLETE SPECIFICATION

A Method of Etching the Surface of a Semiconductor or an Electric Device comprising said Semiconductor

We, TOKYO TSUSHIN KOGYO KABUSHIKI KAISHA (known as TOKYO TSUSHIN KOGYO, LTD.), a limited liability company organised under the law of Japan, of No. 351, 6-Chome, Kita-Shinagawa, Shinagawa-Ku, Tokyo-To, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel method of etching the surface of a semiconductor or an electric device comprising said semiconductor and more particularly to a method of etching said surface with a novel etchant.

Hitherto, electro-chemical methods and purely chemical methods have been practised for etching the surface of a semiconductor such as a germanium crystal and an electric device comprising said semiconductor. However, it is very difficult to employ automatically said methods because of the following disadvantages. Since the purely chemical method employs, usually, an etchant containing hydrofluoric acid, nitric acid, and the like, which are strongly corrosive and injurious to the human body, said etchant is inconvenient to handle, and the possibility that the other metal parts composing the device other than the material to be etched will be corroded is a cause for apprehension. For avoiding said disadvantage, it has been customary to protect the device from corrosion by application of a wax, resistive to the corrosive etchant, to the surface of the device, or by pouring a fine stream of the corrosive etchant on only the surfaces to be etched. However, these operations cannot be carried out without troublesome hand operation. On the other hand, the electro-chemical method incurs no apprehension relating to corrosion, but uniform etching of only the surfaces desired to be etched is relatively difficult because of non-uniformity of the electric current distribution in the case of a device of complex geometry or large size. Of course, a well-known method has been to use a cathode of special form in order to make the current distribution uniform, but this method necessitates troublesome hand operations also.

[*Price 3s. 6d.*]

It is an essential object of this invention to provide a novel method of etching the surface of a semiconductor such as a germanium product or an electric device composed of said semiconductor without the accompaniment of the above-mentioned disadvantages in the conventional methods.

According to one aspect of the invention we provide a method of etching the surface of a semiconductor such as germanium or an electric device comprising said semiconductor, said method consisting of treating the surface to be etched with an etching solution composed of hydrogen peroxide, caustic alkali and a metal sequestering agent of a kind adapted to prevent the deposition on the semiconductor of any undesirable metal or metals which might be present in, or introduced into, the solution in ionic form.

According to a more limited aspect of the invention we provide a method of etching the surface of semiconductor such as germanium or an electric device comprising said semiconductor according to claim 1, in which the etching solution is prepared by mixing 0.01—20% of caustic alkali such as caustic soda, caustic potash, or the like, 0.1—3% of hydrogen peroxide, and 0.01—10% of a metal ion inhibitor such as potassium cyanide, sodium cyanide, EDTA (ethylen-diamine-tetraacetic acid), polyphosphoric acid, or the like.

An illustrative description will be considered in the case of a germanium crystal. The hydrogen peroxide acts to convert the surface germanium into germanium oxide by oxidisation of said germanium, the caustic alkali at once reacts with said germanium oxide to remove said oxide as a soluble alkali germanate, and the metal sequestering agent prevents the hydrogen peroxide from decomposing which would otherwise be caused by catalytic action

of ions of any heavy metals which may be present, and also prevents the deposition of the heavy metal or metals on the germanium surface which would cause deterioration of the excellent properties of the semiconductor.

The pressure of ions of heavy metals in the etching solution may arise in a number of ways. For example the ions may be derived from metal parts, such as wire leads, forming part of the semiconductive device under treatment, also they may originate from within the body of the semiconductor as etching proceeds. In addition they may accidentally introduced into the etching solution from contaminated containers or instruments, or from the use of water deionised by ion exchange and which may still contain residual iron and copper ions to an extent sufficient to affect the process.

Nickel, cobalt, lead, tin, copper, and the like, are the metals mainly used in electric devices incorporating semiconductors. These metals are strongly resistive against the weak alkaline liquid and slightly or scarcely corroded by said liquid even when said metals are immersed for a long time in said liquid.

The etchant may be prepared by mixing 0.01—20% of caustic alkali such as caustic soda, caustic potash, or the like caustic alkali such as rubidium or caesium hydroxides, 0.1—30% of hydrogen peroxide, and 0.01—10% of a metal sequestering agent such as potassium cyanide, sodium cyanide, EDTA (ethylen-diamine-tetraacetic acid), poly-phosphoric acid, or the like.

However, the following amounts of the constituents are preferable in view of various factors such as ease of washing with water after etching, and etching rate, life, stability, dangerous property and toxic characteristic of the etchant and from the economical point of view.

Hydrogen peroxide	0.5—20%
Caustic alkali	0.05— 5%
Metal sequestering agent ...	EDTA, 0.01—0.5%

The most preferable etching temperature is found to be in the range between 15°C and 50°C.

Specific example:

The process was carried out with the use of an etchant of the following composition.

H_2O_2	5%
KOH	0.1%
EDTA	0.1%
H_2O	remainder

The results were as follows:

(*a*) P type germanium of 3 Ω – cm was, after lapping of its surface with emery of No. 304 fineness, immersed in the above-mentioned etching solution for thirty minutes at a temperature of 35°C while said solution was stirred to etch the surface of said germanium, and then said germanium was washed with water. The surface recombination velocity of the electrons of said finished surface was about 250—350 cm/sec and very stable. With the surface of the N type germanium, about the same result was obtained.

On the contrary, when the same surface as in this example was etched with CP.4 solution, said velocity was about 200—250 cm/sec.

(*b*) The NPN alloy type germanium transistors constructed by the conventional method, collector diameter and specific resistivity of base material of each of said transistors being, respectively, 1—1.2. mm and 2—4 Ω – cm, were immersed in the above-mentioned etching solution for thirty minutes at a temperature of 35°C while said solution was stirred to etch the surface of said semiconductor, and then said transistors were washed amply with water. The results were as follows.

The cut-off current of each of forty-two pieces among fifty test pieces was below 5 μA at 25V. These results were the same as those obtained by the conventional electrolytic polishing.

(*c*) The case of power transistor:

The NPN alloy type germanium power transistors constructed by the conventional method, collector diameter and specific resistivity of base material of each of said transistors being, respectively, 2—2.2 mm and 2—4 Ω – cm, were immersed in the above-mentioned etching solution for one hour at a temperature of 35°C to etch the surface of the semiconductor, and then said transistors were washed with water. The cut-off current of each of seven pieces among ten test pieces was below 20 μA at 25V.

(*d*) Decrease of the concentration of the etchant due to decomposition thereof by hydrogen peroxide did not occur even after standing fifty hours at a temperature of 45°C.

(*e*) When a germanium semiconductor of P type single crystal construction was etched in the etching solution at a temperature of 35°C while said solution was stirred constantly, the etching rate on (111) surface of the crystal was about 0.6 μ/minute.

(*f*) When an electric device composed of a semiconductor and copper wires was etched by the etchant of this invention, the copper wires caused no unfavourable effects on said device.

In the method of this invention, since the surface etching of the semiconductor or electric device comprising a semiconductor is carried out with such a particular etchant as described above, the operation brings no danger to the human body, and the process progresses smoothly and without corrosion of the other metals, so that handling and etching operations are very simple, and the surface of the etched semiconductor is not adversely affected even when other metals are present with said semiconductor.

Furthermore, this invention is suitable for treating the semiconductor device of various types such as the PNP type, NPN alloy type, grown type and of complex construction.

WHAT WE CLAIM IS:

1. A method of etching the surface of a semiconductor such as germanium or an electric device comprising said semiconductor, said method consisting of treating the surface to be etched with an etching solution composed of hydrogen peroxide, caustic alkali and a metal sequestering agent of a kind adapted to prevent the deposition on the semi-conductor of any undesirable metal or metals which may be present in, or introduced into, the solution in ionic form.

2. A method of etching the surface of semiconductor such as germanium or an electric device comprising said semiconductor according to claim 1, in which the etching solution is prepared by mixing 0.01—20% of caustic alkali such as caustic soda, caustic potash, or the like, 0.1—30% of hydrogen peroxide, and 0.01—10% of a metal ion inhibitor such as potassium cyanide, sodium cyanide, EDTA (ethylen-diamine-tetraacetic acid), polyphosphoric acid, or the like.

3. A method of etching the surface of a semiconductor such as germanium or an electric device comprising said semiconductor according to claims 1 and 2, in which the etching is carried out at a temperature between 15°C and 50°C.

4. A method of etching the surface of a semiconductor such as germanium or an electric device comprising said semiconductor substantially as hereinbefore described.

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Printed for Her Majesty's Stationery Office by J. Looker Ltd., Poole, Dorset. 1959.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.